<International Research Center for Elements Science> Organic Main Group Chemistry

International Research Center for Elements Science – Organic Main Group Chemistry –

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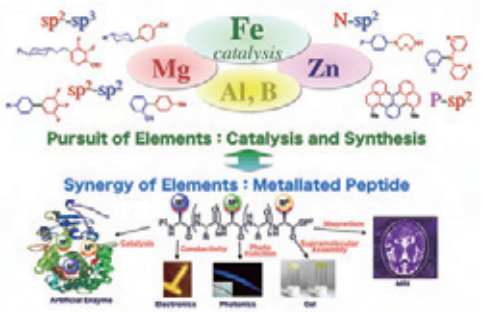
Visitors

Prof KOTORA, Martin	Charles University, Czech Republic, 6 January
Prof LUH, Tien-Yau	Department of Chemistry, National Taiwan University, Taiwan, 29 January
Prof LEE, Hee-Seung	Korea Advanced Institute of Science and Technology, KAIST, Korea, R., 23 February
Prof SHING, Tony K M	Department of Chemistry, The Chinese University of Hong Kong, Hong Kong, China, P. R., 1 June–31 August
Prof MAZET, Clement	Department of Organic Chemistry, University of Geneva, Geneva, Switzerland, 9 July
Prof DOUCET, Henri	Institut Sciences Chimiques de Rennes, Université de Rennes, Catalyse et Organometalliques, Rennes, France, 12 July
Prof ORGAN, Michael G	Department of Chemistry, York University, Toronto, Canada, 8 November

Scope of Research

Our research activity is focused on the development of molecular transformation reactions, which can provide new ways to exploit chemical resources, such as haloalkanes, alkenes, alcohol etc. The present research subjects are (1) metal-catalyzed controlled Carbon–Carbon bond forming reactions by using universal metals such as iron, magnesium and aluminum (2) development of smart materials based on synergistic effect of various metals on artificial peptide (3) understanding and design of synergistic effects of multi-element center interactions for the catalysis with the help of quantum chemical methods and spectroscopy.



Selected Publications

Ito S, Itoh T, Nakamura M: Diastereoselective Carbometalation of Oxa- and Azabicyclic Alkenes under Iron Catalysis, *Angew. Chem. Int. Ed.*, **50,** 454-457 (2011).

Ishizuka K, Seike H, Hatakeyama T, Nakamura M: Nickel-Catalyzed Alkenylative Cross-Coupling Reaction of Alkyl Sulfides, *J. Am. Chem. Soc.*, **132,** 13117-13119 (2010).

Hatakeyama T, Hashimoto T, Kondo Y, Fujiwara Y, Seike H, Takaya H, Tamada Y, Ono T, Nakamura M: Iron-Catalyzed Suzuki-Miyaura Coupling of Alkyl Halides, *J. Am. Chem. Soc.*, **132,** 10674-10676 (2010).

Hatakeyama T, Hashimoto S, Ishizuka K, Nakamura M: Highly Selective Biaryl Cross-Coupling Reactions between Aryl Halides and Aryl Grignard Reagents: A New Catalyst Combination of *N*-Heterocyclic Carbenes and Iron, Cobalt, and Nickel Fluorides, *J. Am. Chem. Soc.*, **131,** 11949-11963 (2009).

Noda D, Sunada Y, Hatakeyama T, Nakamura M, Nagashima H: Effect of TMEDA on Iron-Catalyzed Coupling Reactions of ArMgX with Alkyl Halides, *J. Am. Chem. Soc.*, **131,** 6078-6079 (2009).

KEYWORDS

Carbon–Carbon Bond Formation
Iron Catalyst
Cross-Coupling Reaction
Metallated Peptide
π-Conjugated Molecule

Diastereoselective Carbometalation of Oxa- and Azabicyclic Alkenes under Iron Catalysis

Transition-metal-catalyzed carbometalation of alkenes is a powerful synthetic tool for selective carbon–carbon bond formation. Through sequential electrophilic trapping of the intermediate organometallic species, regio- and stereoselective construction of contiguous sp^3 carbon centers can be achieved in a single-pot procedure. We have developed the iron-catalyzed highly diastereoselective carbometalation of various oxa- and azabicyclic alkenes with arylzinc reagents. The carbozincation products were quenched with acid or trapped with electrophiles, giving the corresponding products in excellent yield. Among a series of novel DPPBz derivatives, electron-deficient ligand was found particularly effective to facilitate the carbometalation and suppress the β-heteroatom elimination.

Figure 1. Iron-Catalyzed Diastereoselective Carbozincation of Oxa- and Azabicyclic Alkenes.

Nickel-Catalyzed Alkenylative Cross-Coupling Reaction of Alkyl Sulfides

Transition metal-catalyzed cross-coupling reactions are powerful tools in organic synthesis. While various electrophilic substrates have been utilized in the cross-coupling reactions, organosulfur compounds have received far less attention among them in spite of the long history. In light of the ample supply of sulfur sources, especially as by-products of refinery, in industrial chemistry, we have explored new reactivity of organosulfur compounds in the cross-coupling reaction and found that alkyl aryl sulfides act as *alkenyl* electrophiles to give the arylation products with the simultaneous installation of an olefinic part in the products. The key to success is the use of a bulky NHC ligand, SIPr, which suppresses the conventional biaryl coupling reaction. The theoretical calculation suggests a concerted mechanism for the *β*-hydride elimination and reductive elimination process from nickel(II) thiolate species, which accounts for the new reactivity of the organosulfur electrophile in the present alkenylative cross-coupling.

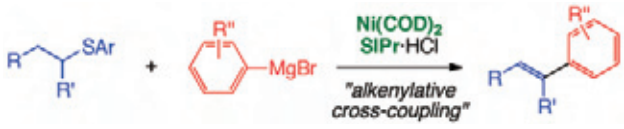


Figure 2. Nickel-Catalyzed Alkenylative Cross-Coupling Reaction.

Programmable Metal Unit Arrangement on Peptides to Create Composition- and Configuration-Controlled Heterometallic Hybrid Materials

This project focuses on the following challenges: i) Development of fundamental methodology for creating composition- and configuration-controlled heterometallic hybrid molecules using metallated-amino acids and peptides as metal units. Chemical synthesis and self-assembly process of the metal units is currently employed, in complementary, to control the composition, 1D/2D array, and 3D configuration of metals on peptides i.e., programmable metal unit arrangements. ii) Exploring the function of heterometallic hybrid molecules. Applications to supramolecular gelators, molecular electronic devices, photochemical devices, advanced catalysts, artificial enzymes, and MRI contrast agents are ongoing with a diverse library of metallated-amino acids and peptides.

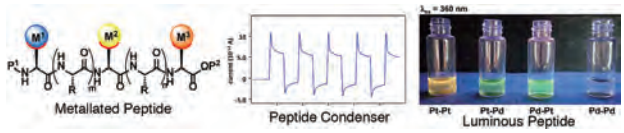


Figure 3. Preparation of Metallated Peptide and Self-Assembly of the Peptide.